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Syntheses, structure and ethylene polymerization behavior of β-diiminato titanium complexes

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Abstract

A series of new titanium complexes bearing β-diiminato ligands $[(Ph)NC(R_1)CHC(R_2)N(Ph)]_2TiCl_2$ (**4a**: $R_1 = R_2 = CH_3$; **4b**: $R_1 = R_2 = CF_3$; **4c**: $R_1 = Ph$, $R_2 = CH_3$; **4d**: $R_1 = Ph$, $R_2 = CF_3$) has been synthesized and characterized. X-ray crystal structures reveal that complexes **4a** and **4c** adopt distorted octahedral geometry around the titanium center. With modified methylaluminoxane (MMAO) as a cocatalyst, complexes **4a**–**d** are active catalysts for ethylene polymerization, and produce high molecular weight polyethylenes. Catalyst activities and the molecular weights of polymers are considerably influenced by the steric and electronic effects of substituents on the catalyst backbone under the same polymerization condition. With the strong electron-withdrawing groups (CF_3) at R_1 or/and R_2 position, complexes **4b** and **4d** show higher activities than complexes **4a** and **4c**, respectively.

Keywords: Titanium complex; Catalyst; Ethylene; Polymerization

1. Introduction

In recent years, a significant amount of attentions have been concentrated on the design and synthesis of highly active, well-defined or single-site transition metal catalysts for olefin polymerization [1–3]. Due to the extensive investigation of complexes with either cyclopentadienyl (Cp) or indenyl (In) ligands, the new non-Cp ligand environment has currently attracted more and more interests. For non-metallocene system with group 4 metals, complexes derived from benzamidine [4,5], diamine [6–9], phosphine-imide [10], pyrrolide-imine [11,12] indolide-imine [13], phenoxy-imine [14–24] and imido [25,26] ligands are reported, many of them show activities comparable to those of metallocene catalysts and in some cases promote living polymerization of α-olefins.

Recently, our group reported a type of titanium catalysts featuring unsymmetrical bidentate β-enaminoketonato ligands for olefin polymerization. By the variation of substituents, we got a highly efficient catalyst, $[(Ph)NC(CF_3)C(H)C(Ph)O]_2TiCl_2$, for the quasi-living ethylene polymerization and ethylene/cyclopentene copolymerization [27–29]. The fact that the variation of the ligand structure may lead to profound changes in the performance of catalyst and the property of polymer prompts us to introduce the bidentate β-diiminato ligand to group 4 transition metal chemistry. β-Diiminato ligands have been known for many years and were initially applied in spectroscopic studies of coordination compounds [30–32]. In the last few years β-diiminato has been used as neutral or monoanionic ligands in wide range of transition metal [33–47], main group element [48–52] and lanthanide [53] complexes, some of which display activity for olefin polymerization.

Although β-diiminato ligand has the isoelectronic relationship with cyclopentadienyl anion, and the steric and

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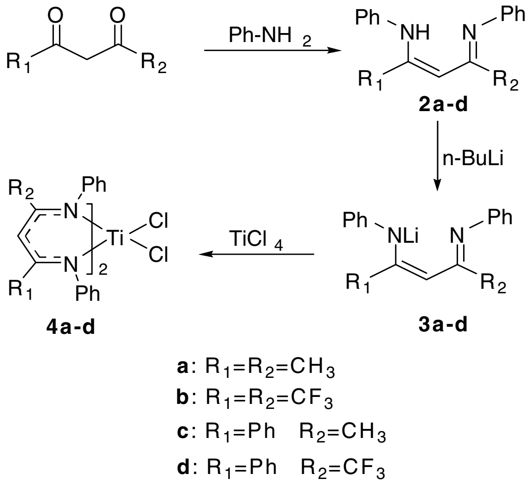
electronic properties of β-diiminato ligand can be readily altered through an appropriate choice of β-diketone, no report on bis(β-diiminato)titanium (IV) catalysts for olefin polymerization has been published. Jin and Novak tried to synthesize (β-diiminato)$TiCl_3$ using $TiCl_4 \cdot 2THF$, but did not come true [40]. Budzelaar [36] and Theopold [37] reported, respectively, Ti(III) complexes which display only low activities towards olefin polymerization. Collins and co-workers [34,39] and Jin and Novak [40] prepared, independently, the zirconium (IV) complexes with β-diiminato ligand, and all the complexes show low to moderate catalytic activities towards olefin polymerization. In previous research work, we found that the introduction of electron-withdrawing group can increase the activity of β-enaminoketonato titanium catalyst [27,29]. This urges us to investigate the effect of the structure of β-diiminato ligand on the performance of titanium catalyst. Herein, we report the syntheses, structures and ethylene polymerization behaviors of $[(Ph)NC(R_1)CHC(R_2)N(Ph)]_2TiCl_2$.

2. Results and discussion

2.1. Synthesis and characterization of complexes

A general synthetic route for new titanium complexes used in this study is shown in Scheme 1. β-Diimine (**2a**–**d**) were obtained in good yields (**2a**, 92%; **2b**, 65%; **2c**, 61%; **2d**, 68%) by the condensation of corresponding β-diketone with aniline in toluene using concentrated hydrochloride or titanium tetrachloride as a catalyst. The desired titanium complexes **4a**–**d** were synthesized under mild conditions in good yields (**4a**, 58%; **4b**, 61%; **4c**, 59%; **4d**, 63%) via the reaction of $TiCl_4$ with 2 equivalents of the lithium salts of β-diimine **3a**–**d** in dry diethyl ether. The resulting complexes were obtained as dark red to brown crystallized solids.



Scheme 1.

The crystals of complexes **4a** and **4c** suitable for X-ray structure determination were grown from dichloromethane–hexane solution. The crystallographic data, collection parameters, and refinement parameters are listed in Table 1, the selected bond lengths (Å) and bond angles (°) for complexes **4a** and **4c** are summarized in Tables 2 and 3, and the molecular structures are shown in Figs. 1 and 2. In solid state, complex **4a** adopts distorted octahedral geometry around the titanium center with *cis* chlorine atoms, in which the N–Ti–N angles involving the bis(β-diiminato) ligands deviate from 90° (N(1)–Ti–N(2) = 84.85(5)°, N(3)–Ti–N(4) = 84.67(5)°). The *trans* influence of the chloride is clearly seen by the shorter Ti–N(3) and Ti–N(1) bond lengths of 2.0994(14) and 2.0857(13) Å compared with the Ti–N(2) and Ti–N(4) distances of 2.1088(14) and 2.1010(13) Å, respectively. Analogously, complex **4c** also displays a distorted octahedral geometry at the metal center with two *cis* chlorine atoms at an angle of 90.67(7)°. The angles involving the metal center and the bis(β-diiminato) ligands deviate from 90° (N(1)–Ti–N(2) = 83.86(11)°). The longer bond distance Ti–N(2) = 2.130(3) Å compared with Ti–N(1) = 2.060(3) Å indicates the similar *trans* influence, but it is stronger than **4a**. Moreover, complex **4c** possesses wider

Table 1
Crystal data and structure refinements of complexes

Complex	4a	4c
Empirical formula	$C_{34}H_{34}Cl_2N_4Ti$	$C_{44}H_{38}Cl_2N_4Ti \cdot 2CH_2Cl_2$
Formula weight	617.45	911.44
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	*Pbcn*
a (Å)	12.9853(11)	11.829(3)
b (Å)	15.3373(13)	19.862(7)
c (Å)	16.3887(14)	18.891(6)
β (°)	106.455(10)	90
V ($Å^3$)	3130.3(5)	4438(2)
Z	4	4
D_{calc} (Mg/m^3)	1.310	1.364
Absorption coefficient (mm^{-1})	0.474	0.591
F(000)	1288	1880
Crystal size (mm)	0.71 × 0.18 × 0.14	0.52 × 0.46 × 0.44
θ Range for data collection (°)	1.86–26.01	2.00–26.02
Reflections collected	17285	5515
Independent reflections (R_{int})	6118 (0.0151)	4380 (0.0336)
Absorption correction	Semi-empirical from equivalents	Psi-scan
Maximum and minimum transmission	0.9354 and 0.7288	0.7809 and 0.7485
Data/restraints/parameters	6118/0/374	4380/2/253
Goodness-of-fit on F^2	1.039	0.977
Final *R* indices [$I > 2\sigma(I)$]: R_1, wR_2	0.0358, 0.0988	0.0549, 0.0665
Largest difference in peak and hole (e $Å^{-3}$)	0.333 and −0.182	0.405 and −0.555

Table 2
Selected bond lengths (Å) and angles (°) for complex **4a**

Bond distance (Å)	
Ti–N(1)	2.0857(13)
Ti–N(2)	2.1088(14)
Ti–N(3)	2.0994(14)
Ti–N(4)	2.1010(13)
Ti–Cl(1)	2.3146(5)
Ti–Cl(2)	2.3124(5)
N(1)–C(7)	1.348(2)
N(1)–C(1)	1.452(2)
Bond angles (°)	
N(1)–Ti–N(3)	87.43(5)
N(1)–Ti–N(4)	90.88(5)
N(3)–Ti–N(4)	84.67(5)
N(1)–Ti–N(2)	84.85(5)
N(3)–Ti–N(2)	168.49(5)
N(4)–Ti–N(2)	86.93(5)
N(1)–Ti–Cl(2)	178.70(4)
N(3)–Ti–Cl(2)	93.57(4)
N(4)–Ti–Cl(2)	90.05(4)
N(2)–Ti–Cl(2)	94.29(4)
N(1)–Ti–Cl(1)	91.20(4)
N(3)–Ti–Cl(1)	94.78(4)
N(4)–Ti–Cl(1)	177.82(4)
N(2)–Ti–Cl(1)	93.91(4)
Cl(2)–Ti–Cl(1)	87.881(19)
C(7)–N(1)–C(1)	115.84(13)
C(7)–N(1)–Ti	121.81(11)
C(1)–N(1)–Ti	122.32(10)

Table 3
Selected bond lengths (Å) and angles (°) for complex **4c**

Bond distance (Å)	
Ti–N(1)	2.060(3)
Ti–N(2)	2.130(3)
Ti–Cl(1)	2.3190(13)
N(1)–C(1)	1.360(4)
N(1)–C(4)	1.438(4)
Bond angles (°)	
N(1)–Ti–N(1)#1	89.19(17)
N(1)–Ti–N(2)#1	92.36(12)
N(1)#1–Ti–N(2)#1	83.86(11)
N(1)–Ti–N(2)	83.86(11)
N(1)#1–Ti–N(2)	92.36(12)
N(2)#1–Ti–N(2)	174.70(18)
N(1)–Ti–Cl(1)#1	175.21(9)
N(1)#1–Ti–Cl(1)#1	90.27(9)
N(2)#1–Ti–Cl(1)#1	92.32(9)
N(2)–Ti–Cl(1)#1	91.41(9)
N(1)–Ti–Cl(1)	90.27(9)
N(1)#1–Ti–Cl(1)	175.21(9)
N(2)#1–Ti–Cl(1)	91.41(9)
N(2)–Ti–Cl(1)	92.32(9)
Cl(1)#1–Ti–Cl(1)	90.67(7)
C(1)–N(1)–C(4)	114.4(3)
C(1)–N(1)–Ti	122.1(2)
C(4)–N(1)–Ti	122.2(3)

Cl–Ti–Cl (90.67(7)°) angle relative to the complex **4a** (Cl–Ti–Cl = 87.881(19)°). The differences in bond lengths and angles probably originate from the steric and electronic effects.

The X-ray structure analyses and the ^{1}H NMR patterns of the titanium complexes suggest that complexes **4a** and**4c** adopt the configuration of *cis* Cl–Cl. However, chelate complexes $[N,N]_2MCl_2$ probably form five isomers, as shown in Scheme 2. Fujita and colleagues calculated the relative formation energies (RFEs) of the titanium complexes bearing two phenoxy-iminato, indolide-iminato or pyrrolide-iminato chelate ligands which are similar to β-diiminato ligands, and found that isomer *cis*-I displays the lowest RFE, and isomers *cis*-II and *cis*-III also exhibit relatively low RFEs, while isomers *trans*-I and *trans*-II show quite high RFEs [11,13,15]. This means that the titanium complexes bearing two β-diiminato chelate ligands tend to form isomer *cis*-I.

The ^{1}H NMR spectra of complexes **4a–d** display a single sharp resonance for the methine proton (=CH–) of the β-diiminato chelate ligands. ^{19}F NMR spectra of **4d** give two peaks at 50.84 and 51.69 with the ratio of 6:1, suggesting that there exits a few isomers of **4d**. ^{19}F NMR spectra of **4b** displaying three peaks also indicates the existence of isomers.

2.2. Ethylene polymerization

With modified methylaluminoxane (MMAO) as a cocatalyst, new titanium complexes **4a–d** have been investigated as the catalysts for ethylene polymerization at room temperature. The results are listed in Table 4. Of the four catalyst systems, complex **4b** exhibited the highest catalytic activity of 312 kg $PE/mol_{Ti} \cdot h$ (Entry 2), followed by complex **4d** (288 kg $PE/mol_{Ti} \cdot h$, Entry 4), **4c** (38.4 kg $PE/mol_{Ti} \cdot h$, Entry 3) and **4a** (2.53 kg $PE/mol_{Ti} \cdot h$, Entry 1). Compared **4b** with **4a**, and **4c** with **4a**, the introduction of strong electron-withdrawing group (CF_3) at R_1 or/and R_2 position is able to considerably increase the polymerization activities with orders of magnitude. Furthermore, with weaker electron-withdrawing group (Ph) at the R_1 position, complex **4b** displays higher activity than complex **4a**. These consequences are consistent with our previous report [24]. The result of ethylene polymerization with $(nacnac)TiCl_2$ (nacnac = [(Ph)NC(Me)CHC(Me)N(Ph)]) is also listed in Entry 11 of Table 4 [37]. Although the activity of complex **4a** is lower than that of $(nacnac)TiCl_2$, complexes **4b** and **4d** display much higher activities towards ethylene polymerization compared with $(nacnac)TiCl_2$.

With the increase of reaction temperature, the activity of catalyst **4b** increases and reaches maximal value of 528 kg $PE/mol_{Ti} \cdot h$ at ca. 25 °C, and then decreases gradually (Entries 2, 8–10 in Table 4) due to thermal decomposition of the catalyst. In addition, the data of entries 2, 5–7 in Table 4 show that the increase of Al/Ti molar ratio from 1000 to 1500 brings on the enhancement in activity, but further increasing Al/Ti molar ratio decreases catalyst activity.

The polyethylenes produced by **4a–d**/MMAO systems exhibit high molecular weights (62.3–410.7 kg/mol). The data listed in Table 4 indicate that the molecular weight

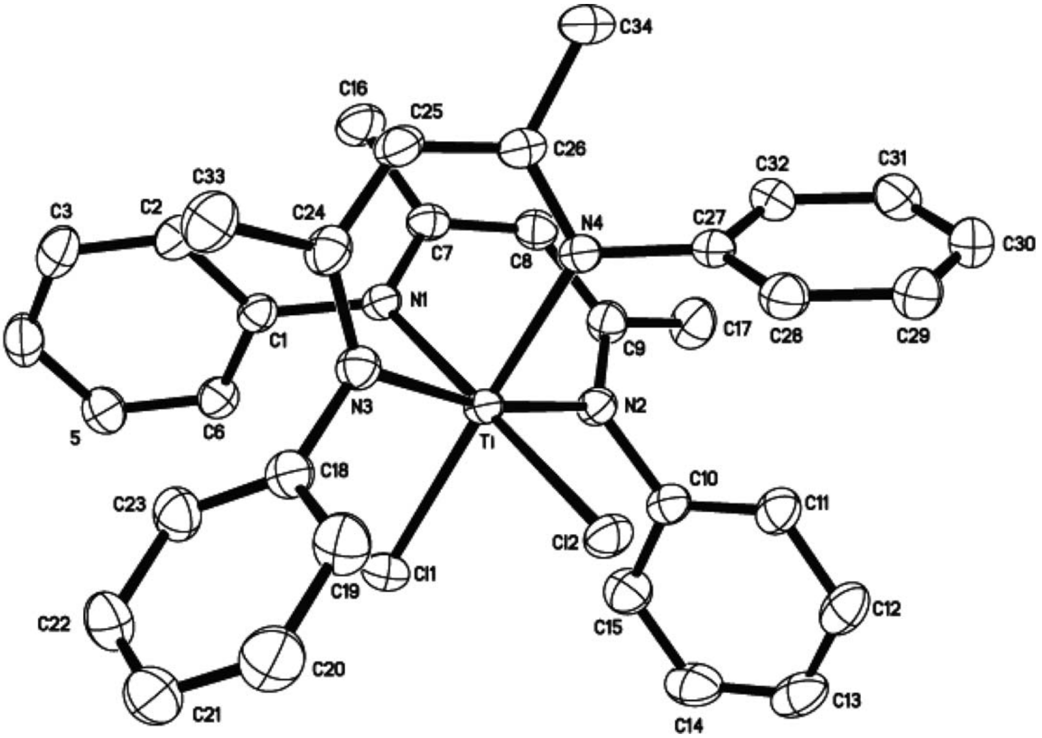


Fig. 1. Molecular structure of complex **4a** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity.

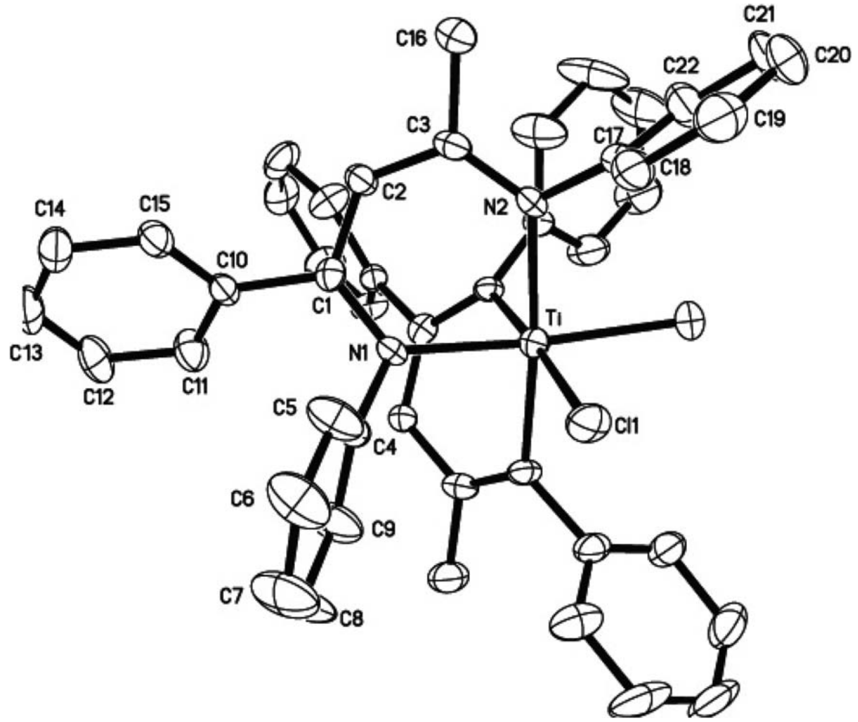
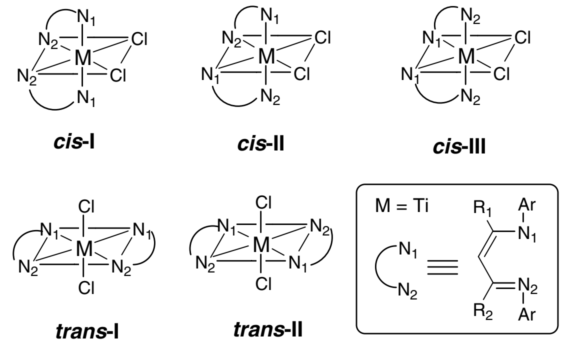


Fig. 2. Molecular structure of complex **4c** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity.

of the polyethylene obtained decreases with the increase of reaction temperature and Al/Ti molar ratio due to increasing β-H elimination reaction and chain transfer reaction to aluminum compounds. Although β-enaminoketonato titanium complex $[(Ph)NC(CF_3)C(H)C(Ph)O]_2TiCl_2$ shows characteristic of quasi-living polymerization [27], β-diiminato titanium catalysts **4a**–**d** produce the polymers with relative broader molecular weight distribution and do not



Scheme 2.

reveal the similar characteristic (Entry 2 in Table 4, PDI = 2.87 for catalyst **4b**; Entry 4, PDI = 2.94 for catalyst **4d**). High-temperature ^{13}C NMR analysis indicates that the polymers possess linear structure with virtually no branching (see Fig. 3), which is in accord with the results of N,N-donor titanium (or zirconium) complexes reported [11–13, 25,40]. Melting temperatures (T_ms values 134.9–137.8 °C) measured by DSC also prove the polymer as typical linear polyethylene.

3. Conclusion

A series of new titanium complexes bearing β-diiminato ligands (**4a–d**) have been synthesized, characterized, and are found to be efficient catalysts for ethylene polymerization with MMAO as a cocatalyst under mild conditions. Polymer yields, catalyst activities as well as molecular weight are considerably influenced by the steric and electronic effects of substituents on the catalyst backbone under the same polymerization condition. With the electron-withdrawing group (CF_3) at R_1 or/and R_2 position, complexes **4b** and **4d** show higher activities than complexes **4a** and **4c**, respectively.

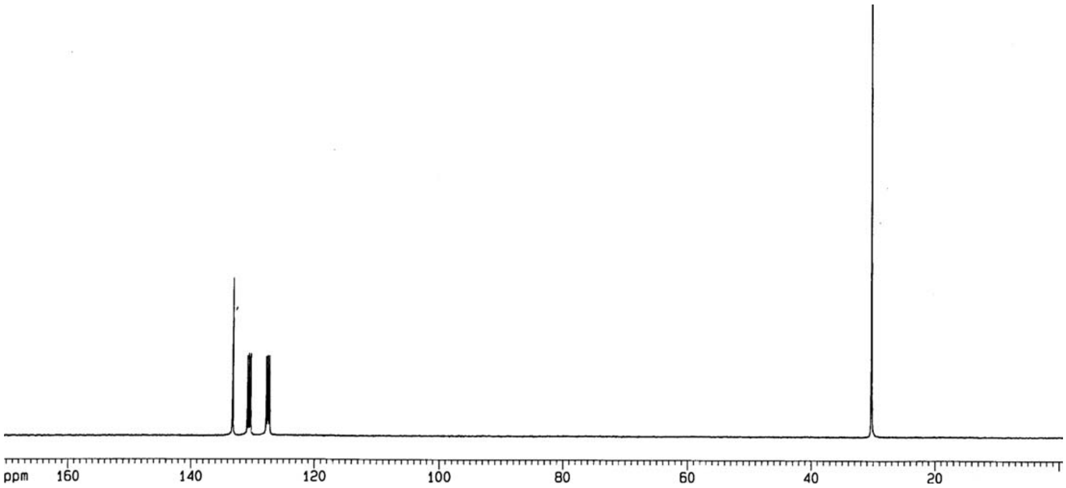


Fig. 3. ^{13}C NMR spectrum of polyethylene prepared with complex **4b**.

Table 4
The polymerization of ethylene with **4a**–**d**/MMAO catalyst systems[a]

Entry	Complex (μmol)	Al/Ti (mol ratio)	*T* (°C)	Pressure (atm)	Reaction time (min)	Polymer (g)	Activity (kg PE/$mol_{Ti} \cdot h \cdot atm$)	T_m[b] (°C)	$\overline{M}_\eta$[c]($\overline{M}_w$[d]) (kg/mol)	$\overline{M}_w/\overline{M}_n$[d]
1	**4a** (10)	1000	25	15	30	0.19	2.53	135.5	410.7	ND
2	**4b** (5)	1000	25	1	10	0.26	312	136.1	210.8 (312)	2.87
3	**4c** (10)	1000	25	15	30	2.88	38.4	135.3	366.3	ND
4	**4d** (5)	1000	25	1	10	0.24	288	137.5	212.6 (305)	2.94
5	**4b** (5)	1200	25	1	10	0.34	408	134.3	189.8 (298)	3.32
6	**4b** (5)	1500	25	1	10	0.44	528	135.7	163.2	ND
7	**4b** (5)	2000	25	1	10	0.38	456	137.2	141.1	ND
8	**4b** (5)	1500	0	1	10	0.15	180	136.8	324.4	ND
9	**4b** (5)	1500	50	1	10	0.23	276	134.1	76.8	ND
10	**4b** (5)	1500	70	1	10	0.07	84	135.0	62.3	ND
11	(nacnac)$TiCl_2$[e]	130	Below 60	20	60	3.4	11.3		818	28.6

[a] Reaction conditions: toluene 50 mL.

[b] Melting temperature determined by DSC.

[c] The intrinsic viscosity was measured in decalin.

[d] Determined by GPC using polystyrene standard.

[e] See Ref. [37].

4. Experimental

4.1. General procedures and materials

All work involving air and/or moisture-sensitive compounds was carried out using standard Schlenk techniques unless otherwise noted. NMR spectra were recorded on a Bruker 300 MHz spectrometer at ambient temperature. ^{1}H NMR and ^{13}C NMR chemical shifts were referenced to residual ^{1}H and ^{13}C signals of the deuterated solvents. ^{19}F NMR chemical shifts were referenced to C_6F_6. The DSC measurements were performed on a Perkin–Elmer Pyris 1 Differential Scanning Calorimeter at a rate of 10 °C/min. The weight-average molecular weight ($\overline{M}_w$) and the polydispersity index (PDI) of polymer samples were determined via high temperature GPC according to the procedure reported previously [27]. Elemental analyses were recorded on an elemental Vario EL spectrometer. The intrinsic viscosity was measured in decalin. At 135 °C using an Ubbleohed viscometer, and the average of molecular weight was calculated by following equation [54]:

$$[\eta] = 4.6 \times 10^{-4} M_{\eta}^{0.73}.$$

1-Benzoylacetone, 1,1,1-5,5,5-hexafluoroacetylacetone and 4,4,4-trifluoro-1-phenyl- 1,3-butanedione were purchased from Aldrich. Diethyl ether, hexane and toluene were refluxed and distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was dried over CaH_2 and distilled before use. Titanium tetrachloride was distilled prior to use. The *n*-butyllithium solution in hexane was purchased from Aldrich. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc.

4.2. Synthesis of ligands **2a–d**

4.2.1. (Ph)NC(CH$_3$)CHC(CH$_3$)NH(Ph) (**2a**) [30]

To a mixture of acetylacetone (10.25 mL, 100 mmol) and aniline (18 mL, 200 mmol) in the 100 mL flask in an ice bath was added concentrated hydrochloride (8.3 mL) slowly with acute stirring and yellow brown solution was formed. After stirring for 12 h, plentiful precipitates were observed. The reaction mixture was filtered and washed with petroleum ether. The solid was dissolved by addition of 8 mL CH_2Cl_2, 50 mL H_2O and 20 mL triethylamine. The aqueous phase was extracted with ether and combined with organic phase, then dried over Mg_2SO_4 and evaporated in vacuo. The crude product was recrystallized from ethanol as yellow crystals in 92% yield.

4.2.2. Compound **2a**

Yield: 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.61 (s, 1H, NH), 7.48–6.63 (m, 10H, PhH), 4.81(s, 1H, =CH), 1.94 (s, 6H, CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 159.97, 146.35, 129.42, 123.81, 123.15, 98.11, 21.43. Anal. Calc. for $C_{17}H_{18}N_2$: C, 81.56; H, 3.38; N, 7.82. Found: C, 81.33; H, 3.45; N, 7.74%.

4.2.3. (Ph)NC(CF$_3$)CHC(CF$_3$)NH(Ph) (**2b**)

$TiCl_4$ (2.2 mL, 20 mmol) in 20 mL of toluene was added dropwise to a solution of aniline (7.3 mL, 80 mmol) in 50 mL of toluene. The resulting mixture was stirred at 90 °C for 30 min followed by the addition of 1,1,1-5,5,5-hexafluoroacetylacetone (4.16 g, 20 mmol). The reaction mixture was stirred overnight, poured into dilute Na_2CO_3 solution, and extracted with methylene chloride. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The residue was dissolved in ether and treated with concentrated hydrochloride at 0 °C. Subsequently, the white precipitate was removed by filtration. The filtrate was washed with dilute Na_2CO_3 solution, dried over anhydrous Na_2SO_4, and evaporated. The crude product was purified by column chromatography on silica gel with petroleum as the eluent, affording the imine compound (Ph)NC(CF_3)CHC(CF_3)NH(Ph) (4.65 g, 13.0 mmol) as a yellow solid in 65% yield. The other ligands **2c–d** were prepared via the same procedure.

4.2.4. Compound **2b**

Yield: 65%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.98 (s, 1H, NH), 7.54–6.84 (m, 10H, PhH), 5.81(s, 1H, =CH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 148.25 (q, $J_{CCF} = 118.8$), 141.64, 127.76, 124.72, 122.01, 119.96 (q, $J_{CF} = 1127.1$), 87.73 (q, $J_{CCCF} = 18.3$). ^{19}F NMR (C_6D_6, 300 MHz): δ 50.86 (CF_3). Anal. Calc. for $C_{17}H_{12}F_6N_2$: C, 56.99; H, 3.38; N, 7.82. Found: C, 66.90; H, 3.25; N, 7.70%.

4.2.5. (Ph)NC(CH$_3$)CHC(Ph)NH(Ph) (**2c**)

Yield: 61%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.52 (s, 1H, NH), 7.84–6.57 (m, 15H, PhH), 5.09 (s, 1H, =CH), 2.13 (s, 3H, CH_3). ^{13}C NMR (300 MHz, $CDCl_3$): δ 164.32, 153.63, 148.36, 141.29, 136.37, 127.72, 127.52, 127.35, 127.22, 127.19, 122.02, 121.06, 120.89, 120,47, 100.45, 20.39. Anal. Calc. for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.68; H, 6.39; N, 8.88%.

4.2.6. (Ph)NC(CF$_3$)CHC(Ph)NH(Ph) (**2d**)

Yield: 68%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.04 (s, 1H, NH), 7.35–6.76 (m, 15H, PhH), 5.40 (s, 1H, =CH). ^{13}C NMR (300 MHz, $CDCl_3$): δ 157.24, 151.03 (q, $J_{CCF} = 108.0$), 147.14, 139.45, 135.19, 128.32, 127.81, 127.44, 127.07, 122.78, 121.81, 119.70 (q, $J_{CF} = 1149.3$), 119.42, 92.34 (q, $J_{CCCF} = 15.6$). ^{19}F NMR (C_6D_6, 300 MHz): δ 50.27 (CF_3). Anal. Calc. for $C_{22}H_{17}F_3N_2$: C, 72.12; H, 4.68; N, 7.65. Found: C, 72.39; H, 4.43; N, 7.68%.

4.3. Synthesis of titanium complexes **4a–4d**

4.3.1. [(Ph)NC(CH$_3$)CHC(CH$_3$)N(Ph)]$_2$TiCl$_2$ (**4a**)

To a stirred solution of compound **2a** (1 g, 4 mmol) in dried diethyl ether (20 mL) at −78 °C was added a 1.6 M *n*-butyllithium hexane solution (2.5 mL, 4 mmol) dropwise over 5 min. The mixture was allowed to warm to room temperature and stirred for 2.5 h. Then, the mixture was added dropwise to $TiCl_4$ (0.22 mL, 2 mmol) in dried diethyl ether (20 mL) at −78 °C with stirring over 30 min. The mixture was allowed to warm to room temperature and stirred for 20 h. The evaporation of the solvent in vacuum yielded a crude product. To the crude product was added dried CH_2Cl_2 (20 mL), the mixture was stirred for 10 min and then filtered. The filtrate was concentrated in vacuo and layered with dried *n*-hexane to gave complex **4a** as a brown solid in 58% yield. The other complexes **4b–d** were prepared by the same procedure with similar yields.

4.3.2. Complex **4a**

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33–7.29 (d, 2H, PhH), 7.16–7.14 (m, 2H, PhH), 7.12(d, 4H, PhH), 6.98–6.94 (d, 2H, PhH), 5.02 (s, 1H, =CH), 2.42 (s, 6H, CH_3). Anal. Calc. for $C_{34}H_{34}Cl_2N_4Ti$: C, 66.08; H, 5.51; N, 9.07. Found: C, 65.91; H, 5.7; N, 9.00%.

4.3.3. $[(Ph)NC(CF_3)CHC(CF_3)NH(Ph)]_2TiCl_2$ (**4b**)

Yield: 61%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30–7.24 (m, 4H, PhH), 7.15 (t, 2H, PhH), 7.10–6.96 (d, 4H, PhH), 5.81 (s, 1H, =CH). ^{19}F NMR (C_6D_6, 300 MHz): δ 50.27 (CF_3, major C_2 isomer), 51.46 (CF_3, minor C_1 isomer), 49.23 (CF_3, minor C_1 isomer).Anal. Calc. for $C_{34}H_{22}Cl_2F_{12}N_4Ti$: C, 48.98; H, 2.64; N, 6.72. Found: C, 49.56; H, 2.32; N, 6.58%.

4.3.4. $[(Ph)NC(CH_3)CHC(Ph)NH(Ph)]_2TiCl_2$ (**4c**)

Yield: 59%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46 (d, 2H, PhH), 7.28–7.26 (m, 6H, PhH), 7.23 (m, 1H, PhH), 7.12 (d, 2H, PhH), 6.96–6.83 (m, 4H, PhH), 5.23 (s, 1H, =CH), 2.63 (s, 3H, CH_3). Anal. Calc. for $C_{46}H_{42}Cl_6N_4Ti$: C, 60.56; H, 4.61; N, 6.14. Found: C, 61.03; H, 4.72; N, 5.99%.

4.3.5. $[(Ph)NC(CF_3)CHC(Ph)NH(Ph)]_2TiCl_2$ (**4d**)

Yield: 63%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.31 (m, 10H, PhH), 7.20–7.09 (m, 10H, PhH), 6.99–6.97 (m, 6H, PhH), 6.75–6.72 (m, 4H, PhH), 5.53(s, 2H, =CH). ^{19}F NMR (C_6D_6, 300 MHz): δ 50.84 (CF_3, major C_2 isomer), 51.69 (CF_3, minor C_1 isomer). Anal. Calc. for $C_{44}H_{32}Cl_2F_6N_4Ti$: C, 62.21; H, 3.80; N, 6.60. Found: C, 62.06, H, 3.94; N, 3.50%.

4.4. Ethylene polymerization under atmospheric pressure

Ethylene polymerization under atmospheric pressure was carried out in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. Toluene (50 mL) was introduced into the nitrogen-purged reactor and stirred vigorously (600 rpm). The toluene was kept at a prescribed polymerization temperature, and then ethylene gas feed was started. After 15 min, the polymerization was initiated by the addition of a heptane solution of MMAO and a toluene solution of complexes **4b** or **4d** into the reactor with vigorous stirring (900 rpm). After a prescribed time, isobutyl alcohol (10 mL) was added to terminate the polymerization reaction, and the ethylene gas feed was stopped. The resulted mixture was added to acidic methanol. The solid polyethylene was isolated by filtration, washed with methanol, and dried at 60 °C for 24 h in a vacuum oven.

4.5. Ethylene polymerization under pressured conditions

Pressured polymerization was carried out at 25 °C under 15 atm ethylene pressure in a 100 mL stainless steel reactor equipped with a propeller-like stirrer. Toluene (50 mL) and a heptane solution of MMAO were introduced into the reactor under ethylene at atmospheric pressure. Ethylene was pumped into the reactor up to 15 atm pressure with stirring vigorously (600 rpm) at 25 °C. Polymerization was initiated by the addition of a toluene solution of the complexes **4a** or **4c** into the reactor with vigorous stirring (900 rpm). After a prescribed time, methanol (5 mL) was added to terminate the polymerization reaction. The reactor was vented and the resulted mixture was added to acidic methanol. The solid polyethylene was isolated by filtration, washed with methanol, and dried at 60 °C for 24 h in a vacuum oven.

4.6. Crystallographic studies

The X-ray crystallographic analyses were performed using crystals **4a** and **4c** with the size 0.71 × 0.18 × 0.14 and 0.52 × 0.46 × 0.44 mm, obtained by recrystallization from dichloromethane/hexane solution at room temperature. The intensity data were collected with the ω scan mode (293 K) on a Bruker Smart APEX diffractometer with CCD detector using Mo Kα radiation ($\lambda = 0.71073$ Å). Lorentz polarization factors were made for the intensity data and absorption corrections were performed using SADABS program [55]. The crystal structures were solved using the SHELXTL program and refined using full-matrix least-squares [56]. The positions of hydrogen atoms were calculated theoretically and included in the final cycles of refinement in a riding model along with attached carbons.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 278834 and 278835 and for the complexes **4a** and **4c**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://ccdc.cam.ac.uk).

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